Sult (°)

c)

aliphatic/aryl-carbonates and cycloalphatic/aryl-carbonates; subjecting said reaction mixture to an elevated temperature sufficient to generate the isocyanate corresponding to said organic formamide compound; and

isolating said isocyanate from said reaction mixture.

27. The process of claim 26, wherein said organic formamide compound is one of the formula

R(NHCHO)_n

where n is an integer from 1 to 10 and R is an organic radical.

The process of claim 27, wherein R comprises an optionally substituted C_{1-20} alkyl, C_{2-20} alkenyl, C_{2-20} alkynyl, C_{4-20} cycloalkyl, C_{4-20} cycloalkenyl, C_{6-30} aryl, C_{7-30} aralkyl, C_{7-30} alkaryl group, a silane or siloxane or oligomer thereof wherein formamide group(s) are bound to an Si-bound hydrocarbon linking group, and wherein each of the above R may contain one or more chain or ring heteroatoms.

- 29. The process of claim 27, wherein R is selected from the group consisting of optionally substituted phenyl, diphenylmethane, and tolyl groups.
- 30. The process of claim 29, wherein R is the 2,4-bis(N-formamide) of toluene diamine.
- 31. The process of claim 26, wherein steps a) and b) are combined such that the reaction temperature of step a) is maintained at a temperature wherein isocyanate is produced directly without prior isolation of O-organocarbonate from said reaction mixture.

- 32. The process of claim 31, wherein the temperature of steps a) and b) are in the range of 150°C to 240°C.
- 33. The process of claim 26, wherein the temperature of step a) is maintained below 190°C and at a first temperature such that no substantial production of isocyanate occurs, said process further comprising:
 - a)i) isolating an intermediate, isocyanate precursor mixture containing a carbamate group-containing reaction product, and thermolyzing said isocyanate precursor mixture at a second, higher temperature to obtain the isocyanate corresponding to said organic formamide.
- 34. The process of claim 33, wherein said isocyanate precursor reaction mixture comprises in excess of 80 mol percent of the carbamate corresponding to said organic formamide, said mol percent based on the total of mols of isocyanate, carbamates and isocyanate/carbamate contained in said isocyanate precursor reaction mixture.
- 35. The process of <u>claim 26</u>, wherein said diorganocarbonate is a diarylcarbonate.
- 36. The process of <u>claim 26</u>, wherein said diorganocarbonate is diphenylcarbonate.
- 37. The process of claim 27, wherein R is aliphatic or cycloaliphatic, said process further comprising adding to said reaction mixture an effective carbamide-cleaving amount of a metal catalyst.

- 38. The process of <u>claim 26</u>, wherein the ratio of mols of diorganocarbonate to organic formamide is greater than 1:1 based on mols of formamide groups.
- 39. The process of claim 26, wherein the ratio of mols of diorganocarbonate to mols of formamide groups is 2:1 to 5:1.
 - 40. The process of claim 26, wherein no catalyst is present.
- 41. The process of claim 26, wherein one or more organic di- or polyamines, an organoformate ester, and diorganophenol carbonate comprise said reaction mixture.
- 42. The process of claim 41, wherein said organo group of said organoformate is the same as at least one of the organo groups of said diorganocarbonate, said organo groups selected from the group consisting of C_{1-20} aliphatic, C_{4-20} cycloaliphatic, C_{6-20} aryl, C_{7-30} aralkyl, and C_{7-30} alkaryl groups, their heteroatom substituted analogs, and mixtures thereof.
- 43. The process of <u>claim 41</u>, wherein said organo groups are selected from the group consisting of C_{1-20} alkyl, C_{5-8} cycloalkyl, and optionally substituted C_{6-10} aryl.
 - 44. The process of claim 41, wherein all organo groups are phenyl.
- 45. The process of claim 41, which is a continuous process wherein organoformate is removed from said reaction mixture and recycled to said reaction mixture with additional organic di- or polyamine.
- 46. A process for the direct manufacture of an organic isocyanate from the corresponding formamide, said process comprising:

- a) reacting an organic formamide containing from 1 to 10 formamide groups per molecule with from 1 to about 10 mol of diorganocarbonate per mol of formamide groups to form a reaction mixture, said reacting taking place at a temperature such that themolysis of products contained in said reaction mixture generates the isocyanate corresponding to said organic formamide;
- b) separating said isocyanate from said reaction mixture.
- 47. The process of claim 46, wherein said isocyanate separated from said reaction mixture also contains partially thermolyzed products containing carbamates corresponding to said organic formamide and/or mixed isocyanate/carbamide compounds corresponding to said organic formamide, said process further comprising:
 - b)i) further thermolyzing said partially thermolyzed products to form additional isocyanate corresponding to said organic formamide; or
 - b)ii) returning said partially thermolyzed products to said reaction mixture; or
 - b)iii) performing both of b)i) and b)ii).
- 48. The process of claim 46, wherein diphenylcarbonate is employed as said diorganocarbonate, reaction takes place in phenol solvent, and said isocyanate separated from said reaction mixture contains phenol and phenol formate ester, said process further comprising recycling said phenol formate ester by reacting said phenol formate ester with an organic amine corresponding to said organic formamide to form said organic formamide.
- 49. The process of claim 46, wherein said organoformate has a boiling point above the decomposition temperature of the O-organocarbonate corresponding to the organic formamide.

50. A continuous process for producing organic isocyanates, said process comprising:

- a) reacting an aryl di- or polyformamide or an amine and formate precursor thereof, with diphenyl carbonate at a temperature at least sufficient to form a reaction mixture containing O-phenylcarbamates corresponding to said aryl di- or polyformamide;
- b) thermolyzing all or a portion of said reaction mixture to generate an isocyanate-containing mixture comprising organic isocyanate(s) corresponding to said aryl di- or polyformamide;
- c) separating said organic isocyanate from said isocyanate-containing mixture to obtain a purified organic isocyanate, and an organic isocyanate depleted mixture c)i);
- d) separating phenol from said isocyanate-containing mixture or from said organic isocyanate-depleted mixture to form a phenol-depleted mixture d)i);
- e) separating carbamates and carbamate/isocyanates from said isocyanatecontaining mixture or from said mixture c)i), or d)i) and further processing said carbamates and carbamate/isocyanates by one or both of
 - e)i) further thermolyzing to form said organic isocyanate(s) corresponding to said aryl di- or polyformamide; or
 - e)ii) cycling said carbamates and/or said carbamate/isocyanates into said reaction mixture of step a),
 - to form a carbamate-depleted mixture e)iii
- f) separating from one or more of said isocyanate-containing mixture, c)i,d)i), or e)iii) phenol formate ester, and
- g) optionally reacting said phenol formate ester with an organic amine to form the formamide corresponding to said organic amine.